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(54) DETERGENT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America of 301, East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to granular detergent compositions containing a particular mixture of anionic and nonionic surfactants, particular amounts of certain organic and/or inorganic salts and moisture. Such compositions are formulated to provide either low or high sudsing and effective detergent performance as well as product stability. Such compositions can be prepared using conventional detergent processing equipment.

Commercial synthetic detergent compositions have for years employed substantial amounts of inorganic phosphate salts as builder materials. Such phosphate builder materials serve to sequester or complex mineral ions commonly found in household tap water in order to prevent such ions from interfering with cleaning performance of the synthetic surfactant in such compositions. Phosphate builders also contribute to the physical stability of granular detergent products.

However, some reactant studies have indicated that the phosphate class of builder materials may present an ecological problem because of the ability of these materials to act as a nutrient that promotes the growth of algae, thereby accelerating the biological ageing (eutrophication) of natural water bodies. As a consequence of the possible harmful effects of the continued use of phosphate builder materials in substantial quantities, attempts have been made to materially reduce or eliminate the need for phosphate salts in commercial detergent compositions.

One method for compensating for the absence of mineral sequestering phosphate builder salts in detergent formulations has been to synthesize compositions containing surfactant systems which are particularly insensitive to mineral hardness in laudering solution. Such surfactant systems have, for example, included relatively mineral insensitive mixtures of anionic and nonionic surfactants. However, since most common nonionic surfactants used in these systems are liquid at room temperature, many formulations containing anionic-nonionic surfactant mixtures have been liquid in nature.

Attempts to achieve acceptable low- or non-phosphate, granular, mixed anionic-nonionic detergent compositions (and the resulting commercial advantages of granular products) by conventional spray-drying techniques have not been entirely successful. Addition of nonionic surfactant to a spray-dried or "blown" anionic surfactant-containing granule creates problems from a performance (sudsing), a processing and a granule stability standpoint.

While the addition of nonionic surfactant to such granules does render the surfactant system less sensitive to dissolved water hardness (i.e. Ca^{++} and Mg^{++} ions) and, hence, more suitable for underbuilt or non-built detergent formulations, such nonionic surfactant addition has a tendency to reduce the foaming and sudsing performance generally desired as a marketing advantage for heavy-duty laundry products. Furthermore inclusion of nonionic surfactants into spray-dried detergent granules aggravates difficulties in processing such granules, i.e. the nonionic surfactant imparts physical properties to detergent composition slurries which render pumping, crutching and spray drying of such slurries extremely difficult. Finally, inclusion of nonionic surfactant into blown detergent

granules (coupled with the elimination or material reduction of hygroscopic phosphate salt levels) generally renders the granular end product more susceptible to caking, pourability problems and stability problems upon storage.

Accordingly, it is an object of the present invention to provide low or non-phosphate, mixed anionic/nonionic surfactant-containing spray-dried detergent compositions which are effective for washing and laundering in mineral-containing water.

It is a further object of the present invention to provide low- or non-phosphate, mixed anionic/nonionic surfactant-containing spray-dried detergent compositions which can have sudsing levels comparable to those of conventional fully-built, high-sudsing, anionic-surfactant containing compositions.

It is a further object of the present invention to provide low- or non-phosphate, mixed anionic/nonionic surfactant-containing detergent compositions in granular form having commercially acceptable caking properties, pourability and storage stability.

It is a further object of the present invention to provide low- or non-phosphate, mixed anionic/nonionic surfactant-containing, spray-dried detergent compositions which can be processed with conventional spray-drying equipment and apparatus.

It has been surprisingly discovered that by combining a particular mixed anionic/nonionic surfactant system with particular organic and/or inorganic salts and moisture in particular essential concentrations, detergent compositions can be formulated which accomplish the above objectives and which are superior in performance, physical characteristics and processability to similar compositions presently known in the art.

According to the invention, we provide a granular spray-dried detergent composition comprising (A) 10% to 30% by weight of a non-soap surfactant system consisting substantially of:

(i) an anionic surfactant which is a sodium or potassium salt of a sulphated fatty alcohol having from 8 to 18 carbon atoms; a sodium or potassium salt of alkyl benzene sulphonic acid in which the alkyl group contains from 9 to 20 carbon atoms; or mixtures thereof; and

(ii) a nonionic surfactant produced by the reaction of one mole of a higher fatty alcohol containing from 10 to 15 carbon atoms with from 3 to 10 moles of ethylene oxide, said nonionic surfactant having a hydrophilic-lipophilic balance of 10 to 13.5;

the weight ratio of the anionic surfactant to the nonionic surfactant being between 2.8:1 and 5:1;

(B) from 10% to 89% by weight of an organic and/or inorganic salt which is an alkali metal carbonate, an alkali metal silicate, a water-soluble alkali metal or alkaline earth metal carboxylate, sulphate or chloride, or mixtures thereof; and

(C) from 1% to 9% by weight of water.

The detergent compositions consist therefore essentially of three component—a particular anionic/nonionic surfactant system, certain organic and/or inorganic salts and moisture. These components, as well as optional components and composition preparation and utilization, are discussed in detail as follows.

From 10% to 30% by weight, preferably from 18% to 25% by weight, of the detergent compositions comprises a particular surfactant system containing a mixture of certain anionic and nonionic surfactants. Total surfactant levels greater than 30% in the instant compositions present processing problems in spray-drying such compositions. Total surfactant levels lower than 10% in the compositions result in lower sudsing and poorer performing compositions.

Surprisingly, only particular anionic and nonionic surfactants in particular amounts can be combined to realize a surfactant system which, when employed in the present compositions, provides the requisite surfactant mineral insensitivity, composition processability and, if desired, high-sudsing performance.

The anionic component of the surfactant system of the present composition can be any of several particular relatively high-sudsing, relatively mineral-sensitive anionic surfactants. Such anionic surfactants are sodium or potassium salts of sulphated fatty alcohols containing from 8 to 18 carbon atoms, the sodium or potassium salts of alkyl benzene sulphonic acids in which the alkyl group contains from about 9 to 20 carbon atoms, or mixtures of these surfactants.

The sulphated fatty alcohol salts, commonly called alkyl sulphates, are produced from natural or synthetic fatty alcohols containing from about 8 to 18 carbon atoms. Natural fatty alcohols include those produced by reducing the glycerides of naturally occurring fats and oils. Fatty alcohols can also be produced synthetically, for example, by the Oxo process. Examples of suitable alcohols which can be employed in alkyl sulphate manufacture include decyl, lauryl, myristyl, palmityl and stearyl alcohols and the mixtures of fatty alcohols derived by reducing the glycerides of tallow and coconut oil.

Specific examples of alkyl sulphate salts which can be employed in the instant detergent compositions include sodium lauryl alkyl sulphate, sodium stearyl alkyl sulphate, sodium palmityl alkyl sulphate, sodium decyl sulphate, sodium myristyl alkyl sulphate, potassium lauryl alkyl sulphate, potassium stearyl alkyl

sulphate, potassium decyl sulphate, potassium palmityl alkyl sulphate, potassium myristyl alkyl sulphate, potassium tallow alkyl sulphate, sodium tallow alkyl sulphate, sodium coconut alkyl sulphate, potassium coconut alkyl sulphate and mixtures thereof. Highly preferred alkyl sulphates are sodium tallow alkyl sulphate, potassium tallow alkyl sulphate, potassium coconut alkyl sulphate and sodium coconut alkyl sulphate.

A second type of relatively high sudsing, relatively mineral-sensitive anionic surfactant useful in the compositions of the instant invention is that of the sodium and potassium salts of alkyl benzene sulphonic acids in which the alkyl group contains from 9 to 20 carbon atoms. These compounds can be straight or branched chained and are described more fully in U.S. Patents 2,220,099 and 2,477,383. Examples of suitable compounds of this type include sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium tetrapropylene benzene sulphonate, potassium decyl benzene sulphonate, potassium undecyl benzene sulphonate, potassium tridecyl benzene sulphonate, potassium tetradecyl benzene sulphonate, potassium tetrapropylene benzene sulphonate and mixtures thereof. Especially preferred for use in the instant detergent compositions are the sodium and potassium salts of straight chain alkyl benzene sulphonic acids in which the alkyl group contains from 11 to 14 carbon atoms. Highly preferred surfactants of this type are sodium linear alkyl benzene sulphonate wherein the alkyl chain length averages about 12 carbon atoms and sodium linear alkyl benzene sulphonate wherein the alkyl chain length averages about 13 carbon atoms.

Mixtures of the above-described alkyl sulphate salts and alkyl benzene sulphonate salts are also operable as the anionic component of the surfactant system of the present compositions.

The second component of the surfactant system of the compositions of the present invention is a nonionic surfactant produced by the condensation of one mole of a higher fatty alcohol containing from 10 to 15 carbon atoms with 3 to 10 moles of ethylene oxide, said nonionic surfactant having a hydrophilic-lipophilic balance (HLB) of from 10 to 13.5. Surprisingly only nonionic surfactants falling within these ranges provide acceptable sudsing performance.

Examples of such nonionic surfactants include the condensation product of one mole of lauryl fatty alcohol with about 6 moles of ethylene oxide, the condensation product of one mole of decyl fatty alcohol with about 4 moles of ethylene oxide, the condensation product of one mole of tridecyl alcohol with about 6 moles of ethylene oxide, the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 5 moles of ethylene oxide, the condensation product of one mole of tridecyl alcohol with about 8 moles of ethylene oxide, the condensation product of one mole of coconut fatty alcohol with 6 moles of ethylene oxide, the condensation product of one mole of coconut fatty alcohol with about 7 moles of ethylene oxide, and the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 9 moles of ethylene oxide.

Examples of commercially-available nonionic surfactants of the type operable in the instant invention include: Tergitol 15-S-7 and Tergitol 15-S-9 (condensates of C_{11-15} linear secondary alcohols with, respectively, 7 and 9 moles of ethylene oxide), marketed by the Union Carbide Corporation (Tergitol is a Registered Trade Mark); Kyro EOB (C_{11-15} linear secondary alcohols condensed with 9 moles of ethylene oxide) marketed by the Procter & Gamble Company, SynLube TDA-92, (C_{13} alcohol condensed with 8 moles of ethylene oxide) marketed by the Sylvan Chemical Company; and Neodol 23-6.5 (primary, slightly branched C_{12-13} alcohols condensed with 6.5 moles of ethylene oxide) and Neodol 25-7 and Neodol 25-9 (C_{12-15} primary alcohols condensed with, respectively, 7 and 9 moles of ethylene oxide), all marketed by the Shell Chemical Company.

Preferred nonionic surfactants include the condensation products of tridecyl alcohol with 6 moles of ethylene oxide, the condensation product of coconut fatty alcohol with 6.0 moles of ethylene oxide, the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with 9 moles of ethylene oxide, Neodol 23-6.5 and Neodol 25-9, marketed by the Shell Chemical Company, and Tergitol 15-S-9, marketed by the Union Carbide Corporation.

The anionic/nonionic surfactant system employed in the instant detergent compositions contains the above-described anionic and nonionic surfactants in a weight ratio of anionic surfactant to nonionic surfactant of from 2.8:1 to 5:1, preferably about 4:1 when high sudsing performance is desired and about 3:1 when low- or medium-sudsing performance is desired. Anionic/nonionic surfactant ratios within this range provide surfactant systems which are sufficiently mineral insensitive to be employed in non-phosphate detergent formulations, which can provide sudsing performance comparable either to that attained with conventional high-sudsing, fully-built detergent products or with conventional low-sudsing, fully-built detergent products. Such surfactant systems also present minimum processing difficulty during conventional spray-drying operations. Anionic/nonionic ratios greater than those specified above result in

surfactant systems which are too mineral sensitive for use in low- and non-phosphate formulations whereas lower anionic/nonionic ratios than those specified above result in compositions which provide poorer sudsing performance and which are extremely difficult to spray dry.

From 10% to 89% by weight of the detergent compositions, preferably from 40% to 50% by weight, comprises certain organic and/or inorganic salts which serve to improve composition performance and facilitate spray drying of the instant compositions. Suitable organic and/or inorganic salts are alkali metal carbonates, alkali metal silicates, electrolyte salts selected from the group consisting of water-soluble alkali metal and alkaline earth metal carboxylates, sulphates and chlorides, or mixtures of such organic and/or inorganic salts.

Examples of suitable alkali metal carbonates include sodium carbonate, potassium carbonate, lithium carbonate, sodium sesquicarbonate, potassium sesquicarbonate and lithium sesquicarbonate. Sodium carbonate is highly preferred.

Alkali metal silicates are common silicon-containing compounds which are generally available commercially in many different physical and chemical forms. Water-soluble alkali metal silicates may be crystalline or amorphous, hydrated or anhydrous and can have varying ratios of alkali metal oxide (M_2O) to silica (SiO_2) within their structures. Generally such ratios vary on a weight basis from 1:0.5 to 1:5.0. Examples of alkali metal silicates operable in the instant invention include sodium metasilicate, potassium metasilicate, sodium sesquisilicate, potassium sesquisilicate, sodium orthosilicate and potassium orthosilicate. Highly preferred compounds in the instant invention are those sodium silicates having a sodium oxide to silica weight ratio of from 1:2.0 to 1:2.4.

Other suitable organic and/or inorganic salts include electrolyte salts selected from the group consisting of the water-soluble alkali metal and alkaline earth metal carboxylates, sulphates and chlorides. Examples of salts of this type include sodium acetate, potassium acetate, sodium citrate, sodium propionate, sodium nitrilotriacetate, sodium oleate, sodium stearate, sodium salt of coconut fatty acid, sodium salt of tallow fatty acid, potassium chloride, sodium chloride, magnesium sulphate and trisodium sulphosuccinate (described more fully in U.S. Patents 3,328,314, 3,424,690 and 3,533,944).

Preferred electrolyte salts of this type are sodium acetate, potassium acetate, trisodium sulphosuccinate and magnesium sulphate. Highly preferred electrolyte salts are sodium acetate and trisodium sulphosuccinate.

In highly preferred non-phosphate embodiments of the instant detergent composition, mixtures of all three of the above-described types of organic and/or inorganic salts are employed. Generally such mixtures comprise (a) from 40% to 50% by weight of the organic and/or inorganic salt mixture of alkali metal carbonates, (b) from 40% to 50% by weight of the organic and/or inorganic salt mixture of alkali metal silicates having M_2O/SiO_2 weight ratios of from 1:2.0 to 1:2.4 and (c) from 5% to 20% by weight of the organic and/or inorganic salt mixture of electrolyte salts selected from the group consisting of sodium acetate, potassium acetate, alkali metal sulphosuccinate and magnesium sulphate. More preferably, such an organic and/or inorganic salt mixture comprises (a) from 42% to 46% by weight of the organic and/or inorganic salt mixture of sodium carbonate, (b) from 42% to 46% by weight of the organic and/or inorganic salt mixture of sodium silicate having a sodium oxide to silica weight ratio of 1:2.4 and (c) from 10% to 15% by weight of the organic and/or inorganic salt mixture of sodium acetate.

In low-phosphate embodiments of the instant compositions (discussed more fully below), a preferred organic and/or inorganic salt component is wholly or in part an alkali metal silicate or mixtures of such silicates having M_2O/SiO_2 weight ratios of from 1:2.0 to 1:2.4, present to the extent of from 6% to 20% by weight of the composition. More preferably, such a salt is a sodium silicate or mixture of sodium silicates having Na_2O/SiO_2 weight ratios of from 1:2.0 to 1:2.4, present to the extent of from 6% to 13% by weight of the composition.

The main function performed by the above-described organic and/or inorganic salts and salt mixtures is to enable the compositions of the instant invention to be spray dried under conventional granular detergent spray-drying conditions. Detergent formulations employing the above-described organic and/or inorganic salts in the concentrations specified are more easily processed in crutchers and spray-drying towers.

In addition to serving as essential processing aids in the spray-drying of detergent compositions of the instant invention, the alkali metal carbonates and alkali metal silicates also serve to adjust the pH of aqueous laundering solutions of the instant compositions to values within the range of from 9.5 to 10.5 within which range surfactant performance is maximized. Some of the above-described salts such as sodium carbonate, sodium nitrilotriacetate and sodium citrate also serve as detergent builders.

The third essential component of the spray-dried detergent compositions is water or moisture. It has been discovered that detergent granules containing the particular anionic/nonionic surfactant system and par-

ticular organic and/or inorganic salt component described above can contain no greater than 9% by weight moisture if free-flowing, non-caking detergent granules are desired. Accordingly, spray-dried compositions of the invention are dried during conventional spray-drying operations to a moisture content of from 1% to 9% by weight. Preferably, detergent granules of the instant invention contain from 3% to 6% by weight of water.

The detergent compositions can optionally contain, in a low-phosphate embodiment, from 1% to 35%, preferably from 20% to 27%, by weight (as compared with a phosphate content of about 50% by weight in fully-built detergent compositions) of certain water-soluble polyvalent inorganic phosphate salts. Such water-soluble phosphate salts are selected from the group consisting of alkali metal pyrophosphates, alkali metal polyphosphates and alkali metal tripolyphosphates. Examples of phosphate compounds of this type include sodium tripolyphosphate, potassium tripolyphosphate, potassium hexametaphosphate, tetrapotassium pyrophosphate and sodium hexametaphosphate, tetrapotassium pyrophosphate and sodium pyrophosphate. A highly preferred phosphate salt is sodium tripolyphosphate.

As noted above, detergent compositions of the instant invention employing the very particular type of nonionic surfactant specified provide surprisingly high sudsing performance under normal laundering conditions. Such high sudsing could, of course, be reduced or eliminated if desired merely by decreasing the anionic surfactant/nonionic surfactant weight ratio to a value below the essential range specified above, i.e. by increasing the amount of nonionic surfactant in the composition. This means of suds inhibition, however, would compound problems of processing the instant detergent composition. It has been discovered that the high sudsing compositions of this instant invention can be modified to provide lower sudsing performance without reduction in their processability by the optional addition of a particular type of suds-suppressing agent.

Such a suds suppressing agent is selected from the group consisting of fatty acids containing from 8 to 24 carbon atoms and mixtures of such fatty acids. Suitable fatty acids can be obtained from natural sources, for example, plant or animal esters (e.g. palm oil, coconut oil, babassu oil, soybean oil, safflower oil, tall oil, wallflower oil, castor oil, tallow, whale and fish oils, grease, lard, and mixtures thereof. Fatty acids also can be synthetically prepared (e.g. by the oxidation of petroleum or by hydrogenation of carbon monoxide via the Fischer-Tropsch process). Examples of suitable fatty acids for use in the present invention include caproic acid, lauric acid, myristic acid, palmitic acid, stearic acid and palmitoleic acid and the mixtures of fatty acids described more fully in U.S. Patent 2,954,347. Examples of commercially available fatty acids for use as suds suppressing agents in the instant compositions include C-1/5, C-108, C-110, T-10, T-11 and 01-910, all marketed by The Procter & Gamble Company, and Hyfac, a hydrogenated fish oil fatty acid marketed by Emery Industries, Inc.

Preferred fatty acids for use herein include (1) mixtures of fatty acids derived from coconut oil and tallow, i.e. coconut fatty acid and tallow fatty acid, (2) hydrogenated fish oil fatty acid containing from about 17 to 18.5 carbon atoms, and (3) mixtures of said tallow fatty acid and said hydrogenated fish oil fatty acid.

If employed, the fatty acid component of the compositions comprises from 0.5% to 5% by weight of the total composition. Preferably, the fatty acid component comprises from 1% to 4% by weight of the composition.

The detergent compositions of the present invention can also contain a wide variety of non-interfering optional ingredients. Such optional components can, for example, include brighteners; hydrotropes and processing aids such as alkali metal toluene sulphonates, perfumes; bleaching agents such as sodium perborate solids or potassium monopersulphate; soil removal enhances such as polyethylene glycol; enzymes; corrosion inhibitors, anti-redeposition agents; calcium precipitate inhibitors; or colouring agents. Such optional materials can comprise up to about 50% by weight of the present detergent composition.

The low- and non-phosphate granular detergent compositions of the present invention are prepared by spray-drying an aqueous slurry of the above-described detergent composition components. Conventional detergent spray-drying equipment can be utilized in such composition preparation. An aqueous slurry to be spray dried is prepared by admixing in a crutcher the above-described surfactant and organic and/or inorganic salt components with enough water to form a slurry containing from about 64% to 72% by weight solids, preferably about 68% by weight solids. Crutcher temperature is generally maintained between about 130°F. and 195°F., preferably about 180°F. for non-phosphate embodiments; preferably about 145°F. for low-phosphate embodiments. Such a slurry is pumped to a conventional spray-drying tower wherein the material is spray dried into granular particles containing the requisite 1% to 9% by weight or moisture content. Preferred methods and apparatus for spray-drying the instant compositions are described in U.S. Patents 3,629,951 and 3,629,955.

Compositions of the present invention are employed by dissolving them in aqueous washing or laundering solution to the extent of

from 0.01% to 2% by weight. Preferably, such compositions are utilized in water to the extent of from 0.06% to 0.18% by weight. This preferred concentration is approximated when about 0.5 to 1.5 cups of the instant detergent composition are added to the 17—23 gallons of water generally held by commercially-available washing machines. Washing solution pH provided by the instant composition generally varies between 9.5 and 10.5. Soiled fabrics or other articles are added to laundering liquor and cleansed in the usual manner.

The granular low- and non-phosphate, spray-dried detergent compositions of the instant invention are illustrated by the following examples:

EXAMPLE I

A spray-dried detergent composition is prepared having the following composition:

Component			Wt. %
Surfactant system			22%
Sodium tallow alkyl sulphate	18%	wt. ratio anionic/nonionic= 4.5:1	
Condensation product of one mole of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 9 moles of ethylene oxide (HLB=13.3)	4%		
Sodium carbonate			74%
Water			4%

Such a composition provides excellent fabric laundering performance when employed under conventional home laundering conditions in laundering liquor of 5 grains/gallon hardness with a composition concentration in laundering liquor of about 0.12% by weight. Under such conditions sudsing performance of the Example I composition compares favourably with that of conventional, fully built, high-sudsing anionic detergent formulations. Such a composition is pourable and is prepared with conventional spray-drying apparatus.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example I composition, the sodium tallow alkyl sulphate is replaced with an equivalent amount of potassium tallow alkyl sulphate, sodium coconut alkyl sulphate, potassium coconut alkyl sulphate, sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium tetrapropylene benzene sulphonate, potassium decyl benzene sulphonate, potassium undecyl benzene sulphonate, potassium tridecyl benzene sulphonate, potassium tetradecyl benzene sulphonate or potassium tetrapropylene benzene sulphonate.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example I composition, the condensation product of a mixture of alcohols having 11 to 15 carbon atoms with 9 moles of ethylene oxide is replaced with an equivalent amount of the condensation product of tridecyl alcohol with about 6 moles of ethylene oxide (HLB=11.4), the condensation product of coconut fatty alcohol with about 6 moles of ethylene oxide (HLB=12.0), Neodol 23-6.5 (HLB=12), Neodol 25-9 (HLB=13.1) or Tergitol 15-S-9 (HLB=13.3).

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example I composition, the sodium carbonate is replaced with an equivalent amount of sodium metasilicate, potassium metasilicate, sodium sesquisilicate, potassium sesquisilicate, sodium orthosilicate, potassium orthosilicate, sodium sesquicarbonate, potassium carbonate, sodium acetate, sodium propionate, potassium acetate, sodium nitrilotriacetate, magnesium sulphate, sodium citrate, sodium salt of tallow fatty acid, sodium chloride, or mixtures of (a) sodium silicate (r=1:2.4), (b) sodium carbonate and (c) sodium acetate.

EXAMPLE II

A phosphate-free, spray-dried detergent composition is prepared having the following composition:

Component			Wt. %
Surfactant System			24.7%
Sodium linear alkyl benzene sulphonate wherein the alkyl group averages about 11.8 carbon atoms in length	20%	wt. ratio anionic/nonionic= 4.26:1	
Condensation product of one mole of coconut fatty alcohol with about 6 moles of ethylene oxide (HLB=12.0)	4.7%		
*Sodium silicate (Na_2O/SiO_2 1:2.4)	wt.ratio=		20.0%
*Sodium carbonate			20.0%
*Sodium acetate			5.0%
**Sodium sulphate			22.1%
Sodium toluene sulphonate			2.0%
Water			4.0%
Minors			balance

*The essential organic and/or inorganic salt component of the above-described Example II is a mixture of sodium silicate, sodium carbonate and sodium acetate of the following composition: sodium silicate—44.5% by weight of the organic and/or inorganic salt mixture; sodium carbonate—44.5% by weight of the organic and/or inorganic salt mixture; sodium acetate—11.1% by weight of the organic and/or inorganic salt mixture.

**Although sodium sulphate is an electrolyte salt as defined above, it is not preferred as an essential component of the instant composition and is generally present chiefly only as a by-product of surfactant preparation. The preferred mixture of essential organic and/or inorganic salts in the Example II composition, therefore, consists only of the carbonate-silicate-acetate mixture.

Such a composition provides excellent fabric laundering performance when employed under conventional home laundering conditions in a laundering liquor of 5 grains/gallon hardness with a composition concentration in laundering liquor of about 0.12% by weight. Under such conditions, sudsing performance of the Example II composition compares favourably with that of conventional, fully-built, high-sudsing anionic detergent formulations. Such a composition is readily pourable and storage stable and is prepared with conventional spray-drying apparatus.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example II composition, the sodium linear alkyl benzene sulphonate is replaced with an equivalent amount of sodium tallow alkyl sulphate, potassium tallow alkyl sulphate, sodium coconut alkyl sulphate, potassium coconut alkyl sulphate, sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium tetrapropylene benzene sulphonate, potassium decyl benzene sulphonate, potassium undecyl benzene sulphonate, potassium tridecyl benzene sulphonate, potassium tetradecyl benzene sulphonate, potassium tetrapropylene benzene sulphonate, or mixtures of these surfactants.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example II composition, the condensation product of coconut fatty alcohol with 6 moles of ethylene oxide is replaced with an equivalent amount of the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 9 moles of ethylene oxide (HLB=13.3); the condensation product of tridecyl alcohol with about 6 moles of ethylene oxide (HLB=11.4); Neodol 23-6.5 (HLB=12.0), Neodol 25-9 (HLB=13.1), or Tergitol 15-S-9 (HLB=13.3).

A composition of substantially similar performance quality, physical characteristics and processability is prepared if, in the above-described Example II composition, there is incorporated about 3% by weight of sodium perborate solids with all other components remaining in the same relative weight proportion.

EXAMPLE III

A low-phosphate, spray-dried detergent composition is prepared having the following composition:

Component			Wt. %
Surfactant System			21.5%
Sodium linear alkyl benzene sulphonate wherein the alkyl group averages about 11.8 carbon atoms in length	17.0%	wt. ratio anionic/nonionic= 3.8:1	
Condensation product of one mole of coconut fatty alcohol with about 6 moles of ethylene oxide	4.5%		
Sodium silicate (Na_2O/SiO_2 wt. ratio= 1:2.4)			6.0%
Sodium silicate (Na_2O/SiO_2 wt. ratio= 1:2.0)			6.0%
Sodium tripolyphosphate			24.0%
*Sodium sulphate			35.3%
Sodium toluene sulphonate			1.7%
Water			4.0%
Minors			balance

*Although sodium sulphate is an electrolyte salt as defined above, it is not preferred as an essential component of the instant composition and is generally present chiefly as a by-product of surfactant preparation. The preferred essential organic and/or inorganic salt in the Example III composition, therefore, consists only of the mixture of sodium silicates having Na_2O/SiO_2 weight ratios of 1:2.0 and 1:2.4.

Such a composition provides excellent fabric laundering performance when employed under conventional home laundering conditions in a laundering liquor of 7 grains/gallon hardness with a composition concentration in laundering liquor of about 0.12% by weight. Under such conditions, sudsing performance of the Example III composition compares favourably with that of conventional, high-sudsing detergent formulations. Such a composition is readily pourable and storage stable and is prepared with conventional spray-drying apparatus.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example III composition, the sodium linear alkyl benzene sulphonate is replaced with an equivalent amount of sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium tetrapropylene benzene sulphonate, potassium decyl benzene sulphonate, potassium undecyl benzene sulphonate, potassium tridecyl benzene sulphonate, potassium tetradecyl benzene sulphonate, potassium tetrapropylene benzene sulphonate, or mixtures of these surfactants.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example III composition, the coconut alcohol condensation product is replaced with an equivalent amount of the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 9 moles of ethylene oxide (HLB=13.3); the condensation product of tridecyl alcohol with about 6 moles of ethylene oxide (HLB=11.4); Neodol 23-6.5 (HLB=12.0); Neodol 25-9 (HLB=13.1) or Tergitol 15-S-9 (HLB=13.3).

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example III composition, the sodium tripolyphosphate is replaced with an equivalent amount of potassium tripolyphosphate, potassium hexametaphosphate, tetrapotassium pyrophosphate or sodium pyrophosphate.

A composition of substantially similar performance quality, physical characteristics and processability is prepared if, in the above-described Example III composition, there is incorporated about 2.9% by weight of sodium perborate solids with all other components remaining in the same appropriate relative weight proportion.

EXAMPLE IV

A low-phosphate, low-sudsing, spray-dried detergent composition is prepared having the following composition:

Component			Wt. %
Surfactant System			12.15%
Sodium Linear alkyl benzene sulphonate wherein the alkyl group averages about 11.8 carbon atoms in length	9.0%	wt. ratio anionic/nonionic= 2.86:1	
Condensation product of one mole of coconut fatty alcohol with about 6 moles of ethylene oxide (HLB=12.0)	3.15%		
Sodium silicate (Na_2O/SiO_2 wt. ratio= 1:2.4)			12.0%
Sodium tripolyphosphate			24.0%
*Sodium sulphate			45.65%
Hydrogenated fish oil fatty acid containing about 18 carbon atoms			2.2%
Water			2.5%
Minors			balance

*Although sodium sulphate is an electrolyte salt as defined above, it is not preferred as an essential component of the instant composition and is generally present chiefly as a by-product of surfactant preparation. The preferred essential organic and/or inorganic salt of the Example IV composition, therefore, consists only of the sodium silicate.

Such a composition provides excellent fabric laundering performance when employed under conventional home laundering conditions in a laundering liquor of 7 grains/Gallon hardness with a composition concentration in laundering liquor of about 0.12% by weight. Under such conditions, sudsing performance of the Example IV composition compares favourably with that of conventional, low-sudsing detergent formulations. Such a composition is readily pourable and storage stable and is prepared with conventional spray-drying apparatus.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example IV composition, the sodium linear alkyl benzene sulphonate is replaced with an equivalent amount of sodium decyl benzene sulphonate, sodium undecyl benzene sulphonate, sodium dodecyl benzene sulphonate, sodium tridecyl benzene sulphonate, sodium tetradecyl benzene sulphonate, sodium tetrapropylene benzene sulphonate, potassium decyl benzene sulphonate, potassium undecyl benzene sulphonate, potassium tridecyl benzene sulphonate, potassium tetradecyl benzene sulphonate, potassium tetrapropylene benzene sulphonate, or mixtures of these surfactants.

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example IV composition, the coconut alcohol condensation product is replaced with an equivalent amount of the condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with about 9 moles of ethylene oxide (HLB=13.3); the condensation product of tridecyl alcohol with about 6 moles of ethylene oxide (HLB=11.4); Neodol 23-6.5 (HLB=12.0); Neodol 25-9 (HLB=13.1) or Tergitol 15-S-9 (HLB=13.3).

Compositions of substantially similar performance quality, physical characteristics and processability are prepared if, in the above-described Example IV composition, the sodium tripolyphosphate is replaced with an equivalent amount of potassium tripolyphosphate, potassium hexametaphosphate, tetrapotassium pyrophosphate or sodium pyrophosphate.

A composition of substantially similar performance quality, physical characteristics and processability is prepared if, in the above-described Example IV composition the hydrogenated fish oil fatty acid is replaced with an equivalent amount of tallow fatty acid or mixtures of tallow fatty acid and hydrogenated fish oil fatty acid containing about 18 carbon atoms.

Detergency performance of compositions of the present invention was compared with that of a commercially-available built granular laundry detergent in a wash and wear test. The test employed is conducted in the following manner: Light-coloured dress shirts, cotton T-shirts and other fabrics such as pillow cases are distributed among various individuals. Each dress shirt and T-shirt is worn for one normal working day under uniform conditions, and the other articles are used for their generally-intended purposes. The soiled clothes and fabrics are then washed in an automatic agitating-type washer, for a period of ten minutes, with detergent solutions at 100°F. The detergents employed are the com-

positions of Examples II, III and IV at a concentration of 0.9 cup per 23 gallons of water and Tide (Registered Trade Mark), a commercially-available built granular detergent marketed by The Procter & Gamble Company, used at varying concentrations. Wash water of 2, 7, and 12 grains/gallon hardness is employed. After washing, the clothes are rinsed (6 spray rinses and one deep rinse) and then dried.

Direct visual comparisons are made by a panel of expert graders between pairs of shirts and fabrics worn and soiled by the same individual. The dress shirts, T-shirts and other fabrics used are graded on the degree of whiteness and the degree of cleaning obtained, paying particular attention on this latter feature to the dress shirt collars and cuffs and pillow cases. For purposes of this invention, the term "cleaning" or "cleanliness" measures the ability of a washing composition to remove actual soil lines or deposits such as at crease lines of collars and cuffs and on pillow cases where the soil has had an opportunity to become deeply embedded. Whiteness, on the other hand, is a more general concept which measures the ability of the cleaning composition to whiten areas which are only slightly or moderately soiled. The relative cleaning effectiveness of each detergent composition in each area is graded visually on a nine point scale under artificial light wherein the highest grade is assigned to the relatively best performance obtained.

Based upon such comparisons, it is found that the compositions of Example II, III and IV of the instant invention provide cleaning and whitness performance comparable to that of equivalent amounts of the commercial detergent, Tide.

The unusual sudsing consistency of the instant detergent compositions is demonstrated by means of a suds height evaluation test. The compositions of Example II and III, described above, and two commercially-available built granular detergent compositions, Tide and Cheer (Registered Trade Mark), both marketed by The Procter & Gamble Company, are utilized under varying conditions of wash water temperature, water hardness, detergent concentration, and soil loads in a General Electric top-loading automatic washer in a standard laundering operation. After 2, 5, 8 and 10 minutes, suds heights for each washing solution tested are measured in inches and averaged for at least 24 runs under each set of conditions. Product concentration varies from 1/2 to 1-1/2 cups of detergent per 23 gallons wash water; water hardness is varied from 0.5 grain/gallon to about 14 grains/gallon; soil load is varied from moderate to very heavy; wash water temperature is varied from about 70°F. to about 140°F.

Over this wide variety of washing conditions, sudsing performance of the Example II and III compositions compares favourably with that of the commercial detergents, Tide and Cheer, with the Example II composition demonstrating less susceptibility to change in the varying conditions than the commercial detergents Tide and Cheer.

The unexpected high-sudsing consistency realised by utilizing the particular nonionic surfactants specified above in the instant compositions is demonstrated by comparing in the above-described sudsing performance test sudsing of the Example II composition described above and an identical composition utilizing a different nonionic surfactant. When the coconut fatty alcohol condensation product of the Example II composition is replaced with an equivalent amount of another ethoxylated fatty alcohol, i.e. the condensation product of 1 mole of tallow fatty alcohol with about 11 moles of ethylene oxide (HLB=12.98, average chain length=17.4 carbon atoms), high-sudsing performance and consistency is significantly poorer.

Sudsing performance of a low-sudsing embodiment of the present invention is also demonstrated by the above-described sudsing test. In such testing, the sudsing performance of the composition of Example IV is compared with sudsing performance of a commercially-available, low-sudsing detergent product, Dash (Registered Trade Mark), marketed by The Procter & Gamble Company. In such testing, the low-sudsing performance of the Examples IV composition compares favourably with that of the commercial formulation Dash.

Determination of the storage stability of the detergent compositions is made by means of a storage stability test. Granular compositions tested are packed into outside waxed laminated and polylaminated cartons containing various types of closures and are stored in constant temperature-humidity chambers for various intervals of time. Such chambers generally are maintained under conditions varying from ambient temperature and humidity to the rather severe temperature-humidity conditions of 80°F. and 80% relative humidity. At specific intervals of time, compositions being tested are removed from the constant temperature-humidity environments and tested to determine caking and pourability properties after such storage.

Although such testing demonstrates that compositions of the instant invention are slightly poorer in storage stability than commercially-available, fully-built, phosphate-containing surfactant compositions, storage stability of the compositions is still acceptable for commercial use and sale.

WHAT WE CLAIM IS:—

1. A granular spray-dried detergent composition comprising:—

(A) 10% to 30% by weight of a non-soap surfactant system consisting substantially of:

(i) an anionic surfactant which is a sodium or potassium salt of a sulphated fatty alcohol having from 8 to 18 carbon atoms; a sodium or potassium salt of alkyl benzene sulphonic acid in which the alkyl group contains from 9 to 20 carbon atoms; or mixtures thereof; and

(ii) a nonionic surfactant produced by the reaction of one mole of a higher fatty alcohol containing from 10 to 15 carbon atoms with from 3 to 10 moles of ethylene oxide, said nonionic surfactant having a hydrophilic-lipophilic balance of 10 to 13.5;

the weight ratio of the anionic surfactant to the nonionic surfactant being between 2.8:1 and 5:1;

(B) from 10% to 89% by weight of an organic and/or inorganic salt which is an alkali metal carbonate, an alkali metal silicate, a water-soluble alkali metal or alkaline earth metal carboxylate, sulphate or chloride, or mixtures thereof; and

(C) from 1% to 9% by weight of water.

2. A composition in accordance with claim 1 comprising 18% to 25% by weight of the surfactant system; 40% to 50% by weight of the organic and/or inorganic salt; and 3% to 6% by weight of water.

3. A composition in accordance with claims 1 or 2 wherein the anionic surfactant is sodium tallow alkyl sulphate, potassium tallow alkyl sulphate, potassium coconut alkyl sulphate, sodium coconut alkyl sulphate or a sodium or potassium salt of a straight chain alkyl benzene sulphonic acid in which the alkyl group contains from 11 to 14 carbon atoms.

4. A composition in accordance with claim 3 wherein the anionic surfactant is sodium linear alkyl benzene sulphonate with an average alkyl chain length of either substantially 12 carbon atoms or substantially 13 carbon atoms.

5. A composition in accordance with any one of the preceding claims wherein the nonionic surfactant is a condensation product of one mole of tridecyl alcohol with 6 moles of ethylene oxide, a condensation product of one mole of coconut fatty alcohol with 6 moles of ethylene oxide, or a condensation product of a mixture of secondary alcohols having 11 to 15 carbon atoms with 9 moles of ethylene oxide.

6. A composition in accordance with any one of the preceding claims wherein the organic and/or inorganic salt is sodium carbonate, potassium carbonate, sodium metasilicate, sodium sesquisilicate, potassium metasilicate, potassium sesquisilicate, sodium orthosilicate, potassium orthosilicate, sodium sesquicarbonate, sodium acetate, potassium acetate, sodium propionate, sodium nitrilotriacetate, magnesium sulphate, sodium salt of tallow fatty acid, sodium citrate, sodium chloride or mixtures of (a) sodium silicates having an Na_2O/SiO_2 weight ratio of 1:2.0 to 1:2.4, (b) sodium carbonate and (c) sodium acetate.

7. A composition in accordance with claim 6 wherein the organic and/or inorganic salt is a mixture of salts comprising 40% to 50% by weight of alkali metal carbonates; 40% to 50% by weight of alkali metal silicates having M_2O/SiO_2 weight ratios of from about 1:2.0 to 1:2.4, and 5% to 20% by weight of sodium acetate, potassium acetate, alkali metal sulphosuccinate, or magnesium sulphate.

8. A composition in accordance with claim 6 or claim 7 wherein the organic and/or inorganic salt mixture comprises from 42% to 46% by weight of sodium carbonate, from 42% to 46% by weight of sodium silicate having a sodium oxide to silica weight ratio of about 1:2.4 and from 10% to 15% by weight of sodium acetate.

9. A low phosphate detergent composition in accordance with any one of the preceding claims comprising: 6% to 20% of an alkali metal silicate having an M_2O/SiO_2 weight ratio of from 1:2.0 to 1:2.4 or mixtures of such alkali metal silicates to form at least part of the said organic and/or inorganic salt; and 1% to 35% by weight of a water-soluble polyvalent inorganic phosphate salt which is an alkali metal pyrophosphate, an alkali metal polyphosphate or an alkali metal tripolyphosphate; the weight ratio of anionic surfactant to nonionic surfactant being substantially 4:1.

10. A composition in accordance with claim 9 comprising 6% to 13% of the said alkali metal silicate or mixture of silicates.

11. A composition in accordance with claim 9 or claim 10 wherein the phosphate salt is sodium tripolyphosphate, potassium tripolyphosphate, potassium hexametaphosphate, tetrapotassium pyrophosphate or sodium pyrophosphate.

12. A low sudsing composition according to any one of claims 9—11 wherein the weight ratio of anionic surfactant to nonionic surfactant is substantially 3:1, which additionally contains from 0.5% to 5% by weight of a suds suppressing agent which is a fatty acid containing from 8 to 24 carbon atoms or mixtures of such fatty acids.

13. A composition in accordance with claim 12 wherein the suds suppressing agent is coconut fatty acid, tallow fatty acid, hydrogenated fish oil fatty acid containing from about 17 to 18.5 carbon atoms or mixtures of tallow fatty acid and hydrogenated fish oil fatty acid

containing from 17 to 18.5 carbon atoms and is present to the extent of from 1% to 4% by weight of the total composition.

14. A composition substantially as hereinbefore described in any one of the Examples.

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